The Development and Possible Recovery of the Antarctic Ozone Hole

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CHAPTER 1 - INTRODUCTION

Since its prediction and discovery, ozone depletion in the stratosphere over Polar Regions has been a topic of widespread interest and debate. Starting in the late 1970s, when the Antarctic ozone observations began, there has been a dramatic decrease in ozone during the polar spring each year (WMO, 2003). The total amount of column ozone regularly goes below 220 DU[1] in the atmosphere above Antarctica, at which point it is defined as an ozone hole (Newman et al., 2004). Whilst the influences on the mechanisms that cause this dramatic ozone loss each year are many, the essential prerequisites for ozone destruction are stratospheric chlorine and bromine (WMO, 2003).

In the few years after 1979, the depletion of ozone rapidly increased from year to year due to the increased emission of chlorofluorocarbons (CFCs) through anthropogenic industrial activities. The troposphere-stratosphere[2] exchange at low latitudes allows compounds such as CFCs to enter the stratosphere. Once there, these compounds are transported to the poles via Brewer-Dobson[3] circulation (Reid, 2000). Here they have very long lifetimes and they can continuously destroy ozone for several decades.

This one part of the reason, why the effective ban on the emission of CFCs agreed to in “The Montreal Protocol on Substances that Deplete the Ozone Layer” in 1989 (Solomon, 1999) has not yet resulted in a significant reduction of the size of the Antarctic ozone hole. Furthermore, the actual extent of ozone destruction is also influenced by other factors such as the polar vortex, polar stratospheric clouds, temperature, water vapour, aerosols and planetary wave activity, which are highly interdependent. How they contribute to severe ozone depletion over Antarctica and why the recovery of stratospheric ozone is believed to be in progress, although still undetected, will be discussed in this paper.

[1] DU stands for Dobson Units and is a measure of the abundance of a substance in the atmosphere. 220 DU means that the total column ozone in the atmosphere would create a layer of 2.2 mm thickness at standard pressure and temperature (on the surface of the Earth).
[2] The atmosphere is divided into four distinct layers according to the sign of the temperature gradient: the troposphere (≈ 0-15km), the stratosphere (≈ 20-45km), the mesosphere (≈ 50-90km) and the ionosphere (> 95km). Thinner layers of small and reversing temperature gradient, the tropopause (≈ 15-20km), the stratopause (≈ 45-50km) and the mesopause (≈ 90-95km) separate these.
[3] A large scale circulation that transports air from lower tropical altitudes upwards and towards the poles.

CHAPTER 2 - THE CHEMISTRY OF OZONE DESTRUCTION

As mentioned above, the two major substances that actively destroy ozone are bromine (Br) and chlorine (Cl). This happens via three catalytic cycles during which ozone molecules (O_3) are broken down to molecular oxygen (O_2):

(I)
$$ClO + ClO + M \Rightarrow Cl_2O_2 + M$$
$$Cl_2O_2 + hv \Rightarrow Cl + ClO_2$$
$$ClO_2 + M \Rightarrow Cl + O_2 + M$$
$$2 \times (Cl + O_3) \Rightarrow 2 \times (ClO + O_2)$$

net: $2\ O_3 \Rightarrow 3\ O_2$

and

(II)
$$ClO + BrO \Rightarrow Br + Cl + O_2$$
$$Cl + O_3 \Rightarrow ClO + O_2$$
$$Br + O_3 \Rightarrow BrO + O_2$$

net: $2\ O_3 \Rightarrow 3\ O_2$

where M can be any kind of atom or molecule, e.g. aerosols, and allows for conservation of energy and momentum. In Antarctica, approximately 70% of the ozone loss is attributed to the Cl cycle (I) and most of the remaining 30% are accounted for by bromine reactions. Depletion by other radicals, only plays a minor role (Singh, 1995). Another, but much slower, mechanism includes Br and HO-radicals:

(III)
$$BrO + HO_2 \Rightarrow HOBr + O_2$$
$$HOBr + hv \Rightarrow Br + OH$$
$$Br + O_3 \Rightarrow BrO + O_2$$
$$OH + O_3 \Rightarrow HO_2 + O_2$$

net: $2\ O_3 \Rightarrow 3\ O_2$

While trace amounts of Br and Cl have always been in the atmosphere, the anthropogenic emission of CFCs has dramatically increased these abundances, leading to massive ozone depletion. The CFCs are photolyzed in the stratosphere, due to the high ultraviolet radiation levels, forming atomic

chlorine radicals (Zondlo et al. 2000). This form and any other form of Cl that is created during the depletion cycles, is called “active chlorine”[4]. It can become inactive (unable to destroy ozone) when it reacts with nitric acid (HNO_3) or water vapour:

$$Cl_2 + HNO_3 \Rightarrow HCl + ClONO_2 \quad \text{(Eq. 1)}$$

$$HOCl + HNO_3 \Rightarrow H_2O + ClONO_2 \quad \text{(Eq. 2)}$$

where HCl and $ClONO_2$ are referred to as reservoir species of chlorine. Under normal stratospheric conditions, this is the chemically favoured form of Cl. Therefore, special conditions are required to create significant abundances of active Cl. This is explained in more detail in the next Chapter.

Although, Br concentrations in the stratosphere are much smaller than Cl concentrations, Br is more effective at destroying ozone than Cl. This is primarily due to the fact that the relevant reservoir species HBr and $BrONO_2$ are significantly less stable than HCl and $ClONO_2$, and are readily photolyzed in the stratosphere. Hence, almost all Br atoms in the stratosphere are in a form that can destroy ozone (Fahey, 2003). This is taken into account when calculating the effective equivalent stratospheric chlorine EESC = Cl + 50 Br (WMO, 2003), which is the standard measure of the effective amount of ozone depleting substances in the stratosphere.

[4] Cl_2 molecules are also called active, as they are easily photolyzed into two atomic radicals.

CHAPTER 3 - INFLUENCES ON OZONE CHEMISTRY

3.1 POLAR STRATOSPHERIC CLOUDS AND AEROSOLS

Unlike Br, the main form of Cl in the stratosphere are its reservoir species (Fahey, 2003). While the catalytic cycles (I) – (III) can destroy ozone very rapidly, special chemical conditions, which release the Cl from its reservoir, are required for severe ozone loss to occur. These conditions are created by polar stratospheric clouds (PSCs). The presence of these clouds provides a surface on which heterogeneous reactions releasing Cl from its reservoir species can occur (Fahey, 2003).

This is where aerosols come into play. Aerosols are liquid or solid particles in the atmosphere other than clouds and precipitation. In the context of Antarctic ozone depletion, the most important group of aerosols are sulphates. Especially sulphuric acid (H_2SO_4) is important for the formation of PSCs (Kondratyev et al., 2006).

There are three main types of PSCs. Type I (which are further divided into Ia and Ib) form from hydrates of sulphuric acid (H_2SO_4/H_2O). While these hydrates usually contain 60-75% of H_2SO_4 in the lower stratosphere at mid-latitudes, the cold temperatures in the Antarctic winter (below 195K) lead to particles of dilute sulphuric acid with a H_2SO_4-concentration of only 40%. Below 198K nitric acid (HNO_3) can condense onto these particles. The resulting ternary solutions of $H_2SO_4/HNO_3/H_2O$ are the type I PSCs (Tabazadeh et al. 1994). At temperatures below 188K, type II PSCs can form (Brassuer et al. 1999). They consist mainly of frozen water vapour, but aerosols can start the condensation. HNO_3 also condenses onto type II PSCs.

PSCs affect ozone depletion in two ways. First of all, they increase the likelihood for reactive encounters of O_3 and Cl or Br, by serving as reaction surfaces. A molecule of O_3 and a Cl-atom are more likely to “meet” if they are “attached” to the surface of a PSC-particle, than when they are randomly flying through the air. Hence, the fourth reaction of the chlorine cycle (I)

$$2 \times (Cl + O_3) \Rightarrow 2 \times (ClO + O_2) \quad \text{(Eq. 3)}$$

occurs at a higher rate when PSCs are present. The same is true for the equivalent reactions of bromine in the other two important cycles (II) and (III):

$$Br + O_3 \Rightarrow BrO + O_2 \quad \text{(Eq. 4)}$$

Actually, this effect increases the rate of almost all chemical reactions important to the ozone depletion cycles, like the formation of activated chlorine from its reservoir-species (reverse of Eq. 1):

$$HCl\ (solid) + ClONO_2\ (gas) \Rightarrow Cl_2\ (gas) + HNO_3\ (solid) \qquad (Eq.\ 5)$$

The (solid) here means that this molecule is attached to a PSC-molecule.

Secondly, PSCs are extremely important for activating stratospheric Cl. The reservoir species HCl and $ClONO_2$ cannot react with ozone. The activation can occur in several ways, e.g. Eq. 5 or the reverse of Eq. 2. No matter how the Cl is activated, there is, in general, the possibility of the reverse reaction, deactivating it again. This is not the case if PSCs are involved. The HNO_3 in Eq. 5 "freezes" onto the PSC-particle, making a back-reaction impossible (or at least much less likely). This heterogeneous chemistry, and the fact that the polar vortex[5] isolates the air over Antarctica from the "outside world" during winter, leads to the creation of much higher concentrations of Cl_2 molecules in the stratosphere than expected from the "normal" chemical equilibrium of Eq.1. The polar vortex also prevents warmer air from lower latitudes from getting into the polar regions, thereby driving temperatures low enough for PSCs to form (Brassuer et al. 1999).

Additionally, type II PSCs can completely remove HNO_3 from the stratosphere, reducing the probability of chlorine returning to the inactive form $ClONO_2$. When HNO_3 freezes onto the small ice crystals, these can get large enough to "fall" out of the stratosphere to lower altitudes. This physical separation of HNO_3 from active chlorine is called denitrification and is a further relevant factor for ozone depletion (Kirk-Davidoff et al., 1999). It slows down the recovery of depleted ozone after the break-up of the polar vortex in spring, as the return of active chlorine to its reservoir species takes longer when less HNO_3 is present.

Once the sun returns in spring, the Cl_2 molecules are easily photolyzed into ozone-depleting radicals ($Cl_2 + hv \Rightarrow Cl + Cl$), which leads to rapid ozone depletion. Figure 1 illustrates the connection between active chlorine and reservoir species abundances and the low temperatures during Antarctic polar vortex required for the formation of PSCs.

All these effects of PSCs apply accordingly to Br and its reservoir species, HBr and $BrONO_2$.

After the maximum of ozone depletion, which usually occurs at the end of September (Newman et al., 2006), the polar vortex becomes continuously weaker until it eventually breaks down, allowing warmer, ozone rich air from lower latitudes to replenish polar stratospheric abundances and causing activated chlorine to return to its reservoir form. Usually, no more total column

[5] The polar vortex is a constant, circumpolar, westerly wind that builds up autumn, when the sun disappears from the pole and breaks down in (late) spring.

ozone values below 220 DU are measured over Antarctica by December (Fahey et al., 2003).

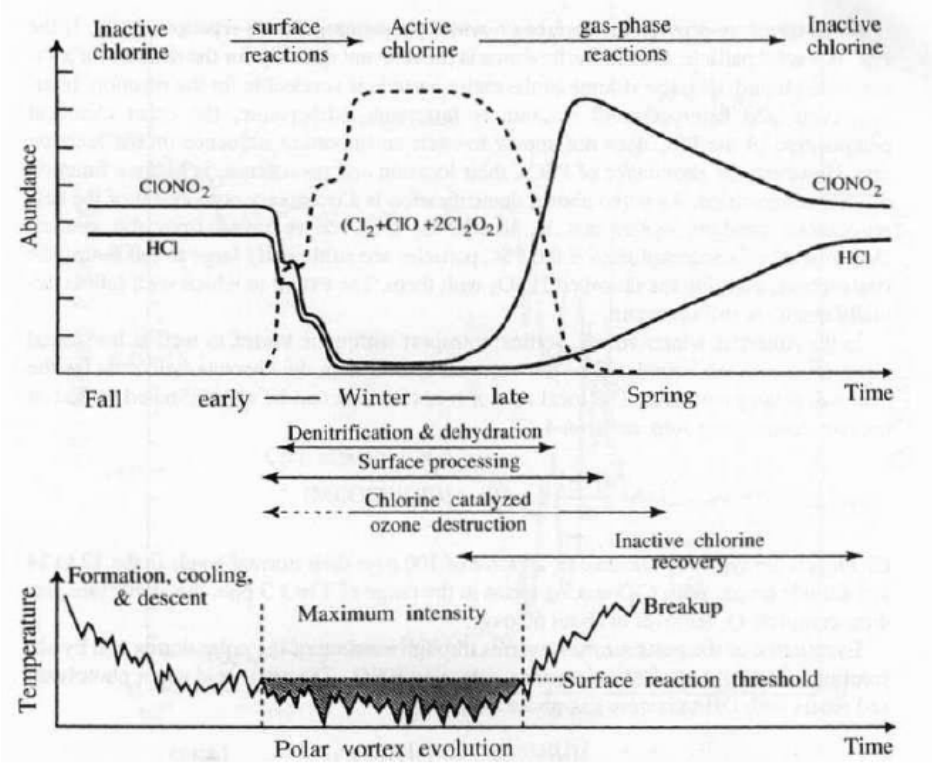

Figure 1: During the Antarctic winter, when the temperatures are cold enough for formation of PSCs, the amount of active chlorine increases drastically whilst the abundances of the reservoir species are simultaneously depleted. These are replenished in spring, as the chlorine is deactivated again. (adapted from Wallace and Hobbs, Ch. 5, 2006).

3.2 PLANETARY WAVES

While the aforementioned influences on ozone depletion occur in a similar manner every year, one other important factor, namely planetary waves, are extremely variable. Planetary waves are oscillations of atmospheric parameters along full circles of longitude. Major causes of these oscillations are large geographic structures, e.g. North-South mountain ranges, which influence the zonal[6] winds, as do large-scale variations of surface heating due to the different reflectivity and absorptance of land and water surfaces. Since these large structures do not change with time, the resulting planetary waves are often quasi-stationary.

One of the most important types of waves are Rossby waves. They are due to the so-called beta-effect (Wallace and Hobbs, Ch. 7, 2006) associated with effects of the Earth's rotation[7]. These waves are preferentially produced at mid-latitudes and they can transport energy and momentum through the atmosphere. This is why they are important for the variability of the size of the Antarctic ozone hole. When Rossby waves transport heat and momentum to the polar stratosphere, they influence the ozone depletion processes because the chemistry of ozone depletion varies non-linearly with temperature, due to the existence of a temperature threshold for PSC formation (Bodeker and Scourfield, 1995).

The most obvious influence of planetary waves on the ozone hole is that they can transport ozone meridionally[8] and vertically and thereby change the amount of ozone in the polar stratosphere directly.

Still, indirect effects are more important. Planetary waves can transport heat toward the poles and reduce the vortex strength through momentum transport and wave breaking (Bodeker and Scourfield, 1995). The latter effects mainly reduce the lifetime and isolation capabilities of the vortex, increasing mixing with undepleted air and hence inducing less ozone deficit and earlier recovery of stratospheric ozone in spring.

[6] Along a circle of longitude.
[7] For more details please refer to the aforementioned Wallace and Hobbs, 2006.
[8] Along a circle of latitude.

CHAPTER 4 – POTENTIAL RECOVERY OF ANTARCTIC OZONE

4.1 REDUCTION OF CFCS AND IT'S LINK TO OZONE RECOVERY

In order to quantify ozone depletion and recovery, the value of 220 DU is used to determine the size of the ozone hole. When ozone depletion occurs in Antarctica the 220 DU contour lies in the region of high ozone gradient and therefore separates the region of depleted air from the undepleted air. The area inside the contour is one measure of ozone hole size (Newman et al., 2004). Another measure, the ozone mass deficit (OMD), is almost equivalent to the area. It is commonly used and refers to the mass of ozone inside the 220 DU contour that is destroyed in spring.

Although there is no certain evidence of ozone recovery – the ozone hole continues to reach close to record sizes every year (WebB, 2006) – it is generally believed that Antarctic spring ozone levels will recover over time in the future. This is because, the overall increase of ozone mass deficit has between 1980 and 1997 has followed the trend of ozone depleting substances (ODSs, measured in EESC) in the stratosphere closely (see Figure 2). Therefore, it is believed, that the reduction of ODSs in the stratosphere, due to the effects of the Montreal Protocol and its amendments, will be result and an equivalent drop of ozone mass deficit over time (WMO, 2003).

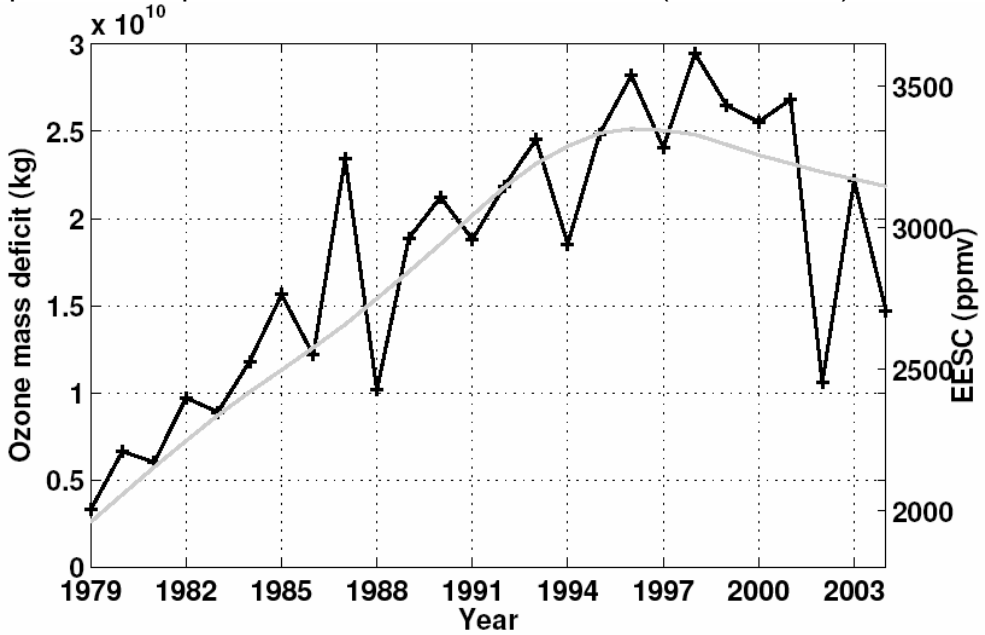

Figure 2: Variability of Antarctic ozone mass deficit in terms of effective equivalent stratospheric chlorine (EESC). While the general trend follows the abundance of ozone depleting substances in the stratosphere (grey line), the (strong) inter annual variations can not be explained this way. (Taken from Huck et al., 2005)

Still, the actual process of recovery is believed to be more complicated. First of all, CFCs take longer to be removed from the stratosphere than they take to get there (Kondratyev, 2006). This is due to the relatively weak coupling between the stratosphere and the troposphere, especially at high latitudes. The intermediate tropopause is relatively stable and does not allow much transport between the layers. Therefore, the projected amount of EESC is not going to reach pre ozone hole levels before the second half of the 20th century (see Figure 3).

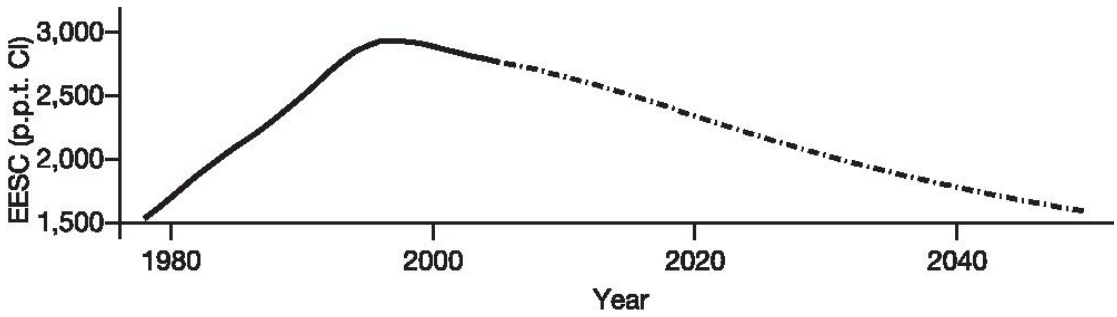

Figure 3: Measured and projected EESC from 1979 to 2050. (Taken from Weatherhead et al., 2006)

Secondly, the highly complex interactions between the many factors that influence ozone depletion mentioned earlier, result in very large year-to-year variations in ozone mass deficit, which can be clearly seen in Figure 2. These are superimposed on any possible reduction of ozone depletion due to the slight decrease in EESC since the maximum around 1996-1998 (Weatherhead et al., 2006). However, recovery is believed to be in progress.

4.2 STAGES OF RECOVERY

Newman et al. (2006) and Weatherhead et al. (2006) both divide the process of recovery into three stages. The first stage is characterized by reduced decline of stratospheric ozone in Antarctic spring, due to the fact that no further ODSs are accumulated in the stratosphere. Newman et al. (2004) Huck et al. (2005) and Yang et al. (2005) have confirmed that this is the current phase of the ozone hole, as it is not significantly growing anymore.

The second stage, referred to as levelling off or turnaround, will display a slow but certain increase of average stratospheric ozone. This can be obscured and delayed by the influences of greenhouse gases, the solar cycle and other intervening effects. Estimates for the first statistically significant detection of ozone increase range from 2008 (Daniel et al., 1995) to 2024 (Newman et al., 2006).

During the third stage, ozone recovery is expected to speed up, eventually leading to a complete disappearance of the ozone hole and total stratospheric ozone levels similar to those before 1980. The exact timing and

form of this recovery is highly disputed. While Newman et al. (2006) propose that 1980 levels of ozone will be reached around 2068 instead of the previous estimate of 2050 (WMO, 2003), Weatherhead et al. argue that it is "unlikely that ozone will stabilize at levels before 1980" (Weatherhead et al., 2006).

4.3 TIMESCALES OF INFLUENCES ON OZONE CHEMISTRY

While the opinions on the final outcome of the decrease in stratospheric ODSs are obviously very disparate, "recovery of ozone is likely to occur in a different atmospheric environment" (Weatherhead et al., 2006), which is why most publications currently focus on the strong variations of ozone mass deficit and the resulting difficulties of actually detecting the beginning recovery. These ascendancies can be roughly divided into three groups, according to the duration of the effects they have on ozone chemistry. They can cause long-term, multi-year and year-to-year variations.

4.3.1 SHORT TERM VARIATONS

Huck et al. (2005) have discovered that the strong inter-annual differences in ozone hole size (or mass deficit) seen in Figure 2 depend largely on mid-latitude planetary wave activity. Particularly in 2002, increased planetary wave activity and planetary wave breaking in the stratosphere occurred (Newman and Nash, 2005). Wave breaking happens when a traveling planetary wave resonates too strongly with a stationary wave, making it unstable and causing it to "break", i.e. release energy and momentum. These events reduced the westerly wind speeds of the polar night jet. This can be seen in Figure 4, which displays the time-evolution of the zonal mean zonal wind, stratospheric temperatures and heat flux in 2002. The average wind speed is decelerated periodically, with a period of about 10 days, due to pulses of energy deposited by planetary waves, raising the temperature and causing a polar vortex that was "one of the smallest in the past two decades" (WMO, #1/2002). This led to reduced occurrence of the low temperatures required for PSC formation, which in turn, are required for the heterogeneous chlorine-chemistry that is essential for Antarctic ozone depletion (Wallace and Hobbs, Ch. 5, 2006).

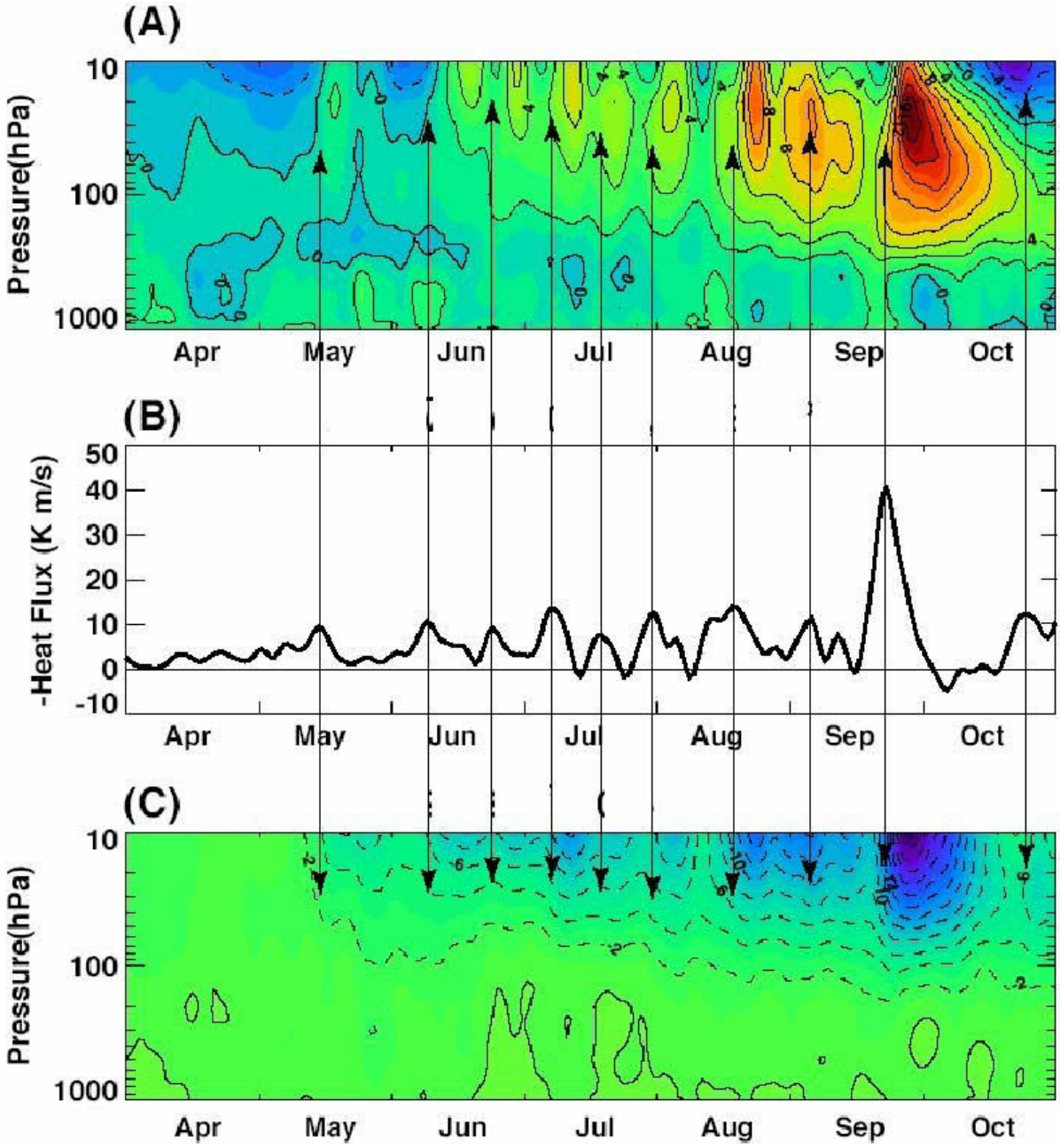

Figure 4: Correlation of changes in stratospheric temperature (A) and zonal mean zonal winds (C) with planetary wave activity (B). Temperatures are averaged for 55-75°S at 50hPa. Contour intervals are 2K. Wave activity is measured through eddy heat flux at 100hPa, averaged for 40-70°S. Daily zonal mean zonal winds are averaged over 20-90°S. Contours are at 2 m/s intervals, the bluer the more easterly. (Taken from Newman and Nash, 2005)

Planetary wave activity is generally higher in the winter hemisphere, because planetary waves can only propagate vertically if the stratospheric zonal wind is westerly and not too strong, which is usually the case in winter. Therefore, the quasi-biennial oscillation (QBO) also effects ozone depletion (Ruzmaikin et al., 2005). The QBO is an oscillation of the average zonal wind direction in the equatorial stratosphere with an average period of 28 months (Baldwin et al., 2001). During the westerly phase of the QBO, planetary wave activity is reduced in both hemispheres, leading to stronger, undisturbed polar

vortices with lower stratospheric temperatures and therefore higher ozone depletion. During the easterly phase of the QBO the level of zero zonal wind is shifted further into the winter hemisphere. Therefore, the effectiveness of wave energy propagation to high altitudes and latitudes is increased, as the planetary waves cannot cross the equator. This again increase the average temperature at the pole, reduces polar stratospheric cloud formation and hence, causes inter annual variations in ozone depletion. The two cases are depicted in Figure 5 (for the Northern hemisphere, but the basic idea is the same in the Southern hemisphere).This so-called Holton-Tan effect was discovered in 1980 (Holton and Tan, 1980).

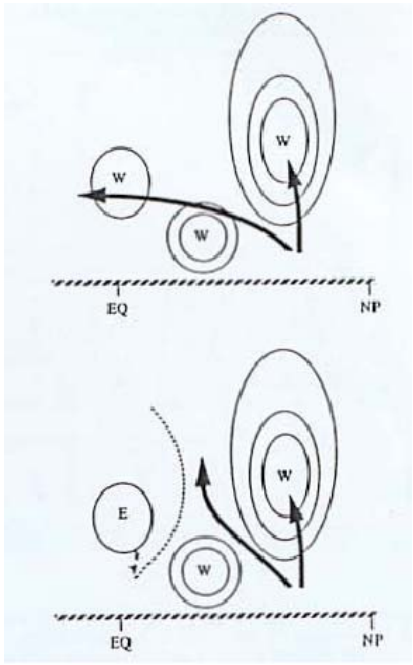

Figure 5: The zonal wind structure in the northern hemisphere winter for the two phases of the QBO (top: westerly, bottom: easterly) in the equatorial lower stratosphere. As planetary waves (arrows) can only propagate when the wind is westerly, they are confined to the hemisphere in the easterly phase. (Taken from Hamilton et al. in Siskind, 2000)

All in all, the inter annual variability of the size of the Antarctic ozone hole is highly correlated with planetary wave activity and therefore strongly influenced by general circulation trends and cycles, such as the QBO.

4.3.2 MEDIUM-TERM VARIATIONS

The sun goes through a regular 11-year cycle, which effects the amount of radiation emitted. This measurably influences stratospheric ozone levels. During a maximum of the solar cycle, the amount of ozone produced in the stratosphere is increased (Benestad, Ch. 6, 2006). Coincidentally, the solar cycle peaked in 1999-2003, the years after maximum ODS-loading. The slight decline in OMD that seems to occur in these years (see Figure 2) is probably due to the solar cycle and not to the decline of ODSs. It could have caused 'uncommonly low' levels of ozone before the cycle maximum and consecutively feign recovery by increasing in solar insolation and ozone production (Zerefos et al., 1997).

By observing over a period of more than two solar cycles, the effects the cycle could potentially be removed from the observations. Unfortunately, the last two solar maxima (before 1999-2003) almost coincided with two major volcanic eruptions, El. Chichón in 1982 and Mt. Pinatubo in 1991. While these eruptions have released large amounts of HCl into the atmosphere, Mankin et al. (1992) and Wallace and Livingston (1992) concluded that this has not led to an increase in polar stratospheric Cl-loading, as almost all the Cl is washed out of the atmosphere before it reaches high altitudes and latitudes. However, volcanic activity does have an indirect effect on ozone depletion, as large amounts of aerosols (mainly sulphur gases) are released. These spread around the whole Earth and can increase the amount of activated chlorine over Antarctica for a few years (Fahey et al., 2003), by the mechanisms mentioned above. As the latest solar maximum occurred during a period of low volcanic activity, the relatively higher ozone values could also result from this lack of volcanic activity compared to previous maxima. Hence, "long-term trends are not expected from solar or volcanic activity" (Weatherhead et al., 2006), but recovery of the ozone hole is going to be very slow in the first few decades and can be obscured or falsely detected due to these effects.

4.3.3 LONG TERM TRENDS

The main expected long-term trend is of course a decline in ozone hole size, due to the decline in ODSs (and accordingly EESC, Figure 3). Currently the average ozone hole size is about 25 million km^2 (averaged over 21-30 September, Newman et al., 2004). While the rate of EESC decline since 1999 is about 1% per year (WMO, 2003), recent elaborate model calculations by Newman et al. (2006) estimate a decline rate of less than 0.3% per year until 2010, followed by slightly increased, but still slow incline until 2020. For the period 2020-2030 further decline of 3-5 million km^2 is expected. This would result in a first statistically significant detection of the recovery in 2024. According to these simulations, 1980 levels of ozone will be reached by 2068 (Newman et al., 2006).

Another long-term effect that has to be considered is that of greenhouse gases (Shindell et al., 1998). While these cause an overall increase in global temperature, the effect is reversed at the poles. There, a cooling by 0.5-1.5 K is predicted by 2010 (Butchart et al., 2000). This has an indirect effect on stratospheric ozone chemistry. The lower temperatures can lead to an increase in PSCs and therefore in OMD. Assuming a continuing trend of decreasing polar temperatures, the date of full recovery will be delayed by about 4 years (Newman et al., 2006). Additionally, the warming due to the greenhouse effect can cause higher precipitation. This would eventually increase the amount of water vapour in the stratosphere. Stratospheric water vapour can also lead to cooling, particularly in the polar regions. Small increases in lower stratospheric water vapour are “likely to have caused a decrease in stratospheric temperature by an amount comparable to that produced by ozone decreases“ (WebA). Finally, possible changes in planetary wave activity are highly uncertain (Austin et al., 2003). However, any kind of climate change that results in reduced wave driving, would cause an increase in ozone depletion, due to lower ozone and temperature advection towards the poles (Newman et al., 2004), and therefore further delay of Antarctic ozone recovery.

CHAPTER 5 - CONCLUSION

While there seems to be consensus that the Antarctic ozone hole is recovering, the exact how and when appears very uncertain. Therefore, more measurements and better models are required to successfully estimate the future of Antarctic ozone. Furthermore, simple time is required in order to estimate currently unknown effects, such as the influence of the solar cycle. But even with extremely accurate data, we can never be certain about our predictions. Due to the high complexity of the interactions in the Antarctic atmosphere itself and with the rest of the global climate, e.g. mid-latitude planetary wave activity, new phenomena, such as the spontaneous break-up of the polar vortex in 2002, are likely to occur.

Anyhow, the rarely occurring fact that almost all scientist agree on something, namely the future recovery of ozone levels in the Antarctic, seems to advocate the hope that this will be the case. For once, human intervention, in the form of “The Montreal Protocol on Substances that Deplete the Ozone Layer”, might actually have worked. Or maybe we are just up for some more surprises?

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